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NEW PATENT APPLICATION

APPARATUS AND METHOD FOR TREATING USED ELECTROLESS PLATING SOLUTIONS

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APPARATUS AND METHOD FOR TREATING USED ELECTROLESS PLATING SOLUTIONS

FIELD OF THE INVENTION

The present invention relates to a process and apparatus for recovering and treating used electroless plating solutions by simultaneous electrolysis and electrowinning.

BACKGROUND

Electroless plating is a commonly used method for introducing a metal coating onto an object. To coat an object with a metal by electroless plating, a metal compound is placed in solution and the elemental metal is subsequently deposited via a chemical reaction. Electroless plating may be used to provide a highly uniform coating of a metal such as nickel, copper, silver, gold, platinum, or palladium on an item. Electroless plating is frequently used in the electronics industry, for example, in the processing of semiconductor wafers.

With time and use, an electroless plating solution will become exhausted and/or contaminated with by-products of the plating process, necessitating its replacement. Spent plating solutions, however, contain metal compounds, with their environmental considerations. Spent plating solutions can also tend to evolve a significant amount of hydrogen gas, presenting an explosion and fire hazard. As a result, a variety of methods have been devised to treat spent plating solutions.

U.S. Pat. No. 6,391,209, the disclosure of which is incorporated herein by reference, describes a number of prior methods for the treatment of spent plating solutions. These include treatment of the solution with an oxidizing agent such as hydrogen peroxide. Another method includes the chemical reduction of the metal and subsequent precipitation of organic complexing agents. Plating solutions may also be treated by exposure to ozone, ultraviolet light, or hydrogen peroxide, or a combination thereof.

U.S. Pat. No. 5,730,856, the disclosure of which is also incorporated herein by reference, describes a method for treating electroless plating solutions by electrolytic oxidation and simultaneous vibration and fluidization by an oscillating stirrer.

Electrochemical cells have also been used to remove metals from metal containing solutions such as electroless plating solutions. U.S. Pat. No. 6,162,333 to Lemon et al., the disclosure of which is incorporated herein by reference, describes such a cell.

SUMMARY

A method for treating an electroless plating solution is provided, the method comprising:

providing a reaction vessel containing an anode, a cathode, a drain and a nozzle, wherein the nozzle is in fluid communication with the drain;

disposing the electroless plating solution in the reaction vessel such that the anode and the cathode are at least partially immersed in the plating solution;

recirculating the plating solution through the reaction vessel by draining the plating solution from the reaction vessel through the drain and subsequently re-injecting the plating solution into the reaction vessel through the nozzle;

placing the anode and cathode in electrical communication with a power source and driving an electrical current through the anode and the cathode to produce a treated plating liquid.

The method may additionally comprise sparging the reaction vessel with an inert gas to create a sparge gas. The method may further comprise removing residual liquid from the sparge gas and venting the sparge gas to a hydrogen gas scrubber. The inert gas may consist essentially of nitrogen gas. Typically, the anode may comprise steel and the cathode may comprise brass.

An apparatus for treating an electroless plating liquid is provided, the apparatus comprising:

a reaction vessel;

a cathode and an anode in electrical communication with a power source, wherein the cathode and anode are disposed in the interior of the reaction vessel;

a drain disposed in the reaction vessel;

a nozzle in fluid communication with the drain, disposed in the reaction vessel such that the nozzle and the drain are separated by the cathode and the anode.

Additionally, the apparatus may additionally comprise a gas sparger in communication with an inert gas source. In such an embodiment, the reaction vessel is typically vented and is in communication with a hydrogen gas scrubber. In one example, inert gas consists essentially of nitrogen gas. The reaction vessel may additionally comprise a heat exchanger.

The apparatus may typically contain a steel anode and a brass cathode.

Additionally, the apparatus may comprise a metal compound-restrictive filter disposed in the reaction vessel such that only liquid essentially free of metal passes through the filter and into the drain.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view of an apparatus for treating an electroless plating liquid

DETAILED DESCRIPTION

One embodiment of an apparatus for treating an electroless plating liquid may be described with reference to Fig. 1. A treatment apparatus 10 comprises a reaction vessel 12. In the interior of reaction vessel 12 is a cathode 14 and an anode 16. Cathode 14 may be brass and anode 16 is any metal that is not oxidized in the process, such as stainless steel. The anode and cathode are in electrical communication with a power source, in certain embodiments, a direct current power source. In one particular embodiment, the current applied is between about 1 and about 10 amperes, although other current levels may also be used.

Also contained within reaction vessel 12 is a drain 18 and a nozzle 20, such as a spray nozzle. Drain 18 is in fluid communication with a first valve 19, which is in turn, in fluid communication with a pump 22. Pump 22 is in fluid communication with nozzle 20 via a second valve 21. Within reaction vessel 12, nozzle 20 and drain 18 are separated by at least the distance between the anode 16 and cathode 14. Reaction vessel 12 may additionally include a sparger in fluid communication with a source of inert gas 30. The inert gas may be, for example, nitrogen, or a noble gas, such as helium or argon. Reaction vessel 12 may also include a vapor trap 24 and a heat exchanger 26 such as a cooling jacket or coiled tube through which cooled water is circulated. If a sparger is present, then a vent 32 is also present. In certain embodiments, vent 32 is preferably in fluid communication with a hydrogen gas scrubber (not shown).

Reaction vessel 12 may optionally comprise a metal compound-restrictive filter immediately upstream of drain 18, thereby concentrating metal compounds in the reaction vessel and preventing them from leaving the reaction vessel. Such a filter can increase the overall efficiency of the treatment process, described in more detail below.

The operation of the apparatus may also be described with reference to Fig. 1. An electroless plating solution is disposed in reaction vessel 12 to a predetermined level. Typically, the anode and cathode will be at least partially immersed in the plating solution to be treated. First valve 19 may be in fluid communication with a plating solution source (not shown) and second valve 21 may be set to distribute liquid from pump 22 to nozzle 20. When a predetermined amount of plating liquid is disposed in reaction vessel 12, valve 19 may be switched to receive liquid from drain 18. Liquid is drained from drain 18, and pumped by pump 22 to nozzle 20, where the liquid is re-injected into reaction vessel 12, thereby providing circulation of the plating liquid during treatment.

During treatment of the plating liquid, the liquid is typically sparged with an inert gas, such as nitrogen, helium or argon. Hydrogen gas that is released during the treatment of the plating liquid, is then swept away with the inert gas to create a sparge gas. Residual amounts of liquid, introduced for example, by liquid injected into the reaction vessel by nozzle 20, and carried with the sparge gas, is removed by vapor trap 24. The at

least partially dried sparge gas is then vented through vent 32, in certain embodiments to a hydrogen gas scrubber (not shown).

An electric current is driven through the anode and the cathode. The current may be a direct current. The anode may be steel, such as stainless steel, and the cathode may be brass. Reducing agents in the plating solution are oxidized at the anode in an electrolysis reaction, decreasing the volume of hydrogen gas generated during treatment, although some hydrogen gas may still be generated from hydrolysis of water or the oxidation of chemical constituents of the plating solution. The metal salt or salts in the plating solution are reduced at the cathode in an electrowinning reaction, causing the metal to plate onto the cathode as the elemental metal. Heat may also be generated during treatment which may be removed by heat exchanger 26. The temperature of the plating liquid may be maintained at a temperature suitable for discharge or further treatment. For example, the plating solution may be maintained at about 50°C or less during treatment. The plating liquid may be further treated, for example, by contacting it with an ion exchange resin after discharge from the system.

The treatment continues for a sufficient time and under sufficient current to oxidize substantially all of the reducing agents. Progress of the reaction may be monitored by oxidation-reduction potential (ORP), colorimetry (if one of the species absorbs visible or ultraviolet light), or other known methods. The treatment may continue under sufficient conditions to oxidize all of the reducing agents according to stoichiometric calculations. For example, if the concentration of a reducing agent is 1 g/liter, and the reducing agent has a molar mass of 58 g/mol and gives up 6 electrons per molecule in the reduction process, complete electrolysis would take 33 minutes at an applied current of 5 amps (assuming 100% current efficiency):

$$1\ \text{g} \div (58\ \text{g/mole}) \times (6\ \text{mole}\ e^-/\text{mole}) \times (96{,}500\ \text{coulombs/mole}\ e^-) \div (5\ \text{coulomb/sec}) \div (60\ \text{sec/min}) = 33\ \text{min}.$$

When treatment is complete, valve 21 is switched to evacuate the treated plating liquid from reaction vessel 12.

EXAMPLE

The following example is set forth to further illustrate an embodiment of the process. The example should not be construed as limiting the process in any manner.

A used electroless plating solution containing cobalt ions as the oxidizing agent and dimethylamineborane (DMAB) as the reducing agent may be treated to prevent plate out and spontaneous production of hydrogen gas as follows.

A used electroless plating solution is placed in reaction vessel 12 and recirculated as described above. Upon application of electric current, the oxidation reaction at the anode is: DMAB $\rightarrow$ DMA + $B(OH)_3$ + $6e^-$; the reduction reaction at the cathode is: Co^{+2} + $2e^-$ $\rightarrow$ Co. The used electroless plating solution is treated until at least a majority of the reducing agent is oxidized and at least a majority of the metal ions are reduced, preferably to an elemental state. Preferably, the reactions are continued until substantially all the of the reducing agent is oxidized and the metal ions are reduced. The used electroless plating solution is then removed from the apparatus.

The result is a used electroless plating solution from which the cobalt ions have been removed and in which the DMAB has been oxidized, so that the solution will not plate out and will not spontaneously produce hydrogen gas.

The present apparatus and process are advantageous over prior systems because they provide for the removal of metals and metal compounds from a plating liquid rapidly and economically with a minimum generation of hydrogen gas.

The entire process may be controlled by a programmable controller, and records data from the process can be sent to a computer which can be used to retrieve the data remotely. The apparatus and process may include a fully automated microprocessor controller which continuously monitors system operation providing fault detection,

pressure and/or temperature control and valve sequencing, ensuring reliability, while minimizing operator involvement.

The apparatus may include system alarms to detect potential hazards, such as temperature or pressure excursions, to ensure system integrity. Alarm and warning conditions may be indicated at the operator interface and may be accompanied by an alarm beeper.

It will be understood that embodiments(s) described herein is/are merely exemplary, and that one skilled in the art may make variations and modifications without departing from the spirit and scope of the invention. All such variations and modifications are intended to be included within the scope of the invention as described hereinabove. It should be understood that any embodiments described hereinabove are only in the alternative, but can be combined.